THE DISTRIBUTION AND NATURE OF-NON-EXTRACTABLE PHOSPHORUS IN SOME GRAY-BROWN PODZOLIC, BRUNIZEM (PRAIRIE), AND PLANOSOL SOIL PROFILES

BY

GEORGE RICHARD BAUWIN

B. S., West Virginia University, 1947
M. S., West Virginia University, 1949

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

On the basis of present knowledge, the native phosphorus in soils can be subdivided into the following general categories: the acid-soluble, adsorbed or replaceable, organic, and insoluble phosphorus forms. As used in this thesis, the term "non-extractable phosphorus" refers to that insoluble fraction of the total phosphorus which was not extracted by the fractionation procedures proposed by Dean, Bray and Kurtz, Ghani, and Williams.

The extractable forms of phosphorus have been studied extensively. Virtually nothing, however, is known concerning the true nature of the non-extractable form which, in many soils, constitutes the largest single fraction of the total soil phosphorus. The objectives of this study were (1) to determine the distribution and amount of non-extractable phosphorus in various horizons of virgin soils, (2) to determine the mineralogical nature of the non-extractable phosphorus in soils, and (3) to establish what factors contribute to the abundance of non-extractable phosphorus in certain soils and its relative absence in others.

Soils and Methods

Residual West Virginia gray-brown podzolic soils developed on acidic gray shales and sandstones, and Illinois soils developed on Peorian loess of Wisconsin age and variable depth were used in this study. The latter were classified into four development series (A, B, C, and D). Group B soils represent the maturity series currently accepted in Illinois. The members of each group vary in maturity, depending on the

relationship between rate of loess deposition and weathering or soil development.

Phosphate fractionation and extractable phosphorus studies were conducted on various horizons of West Virginia and Illinois virgin soils, respectively. The amount of phosphorus extracted when the Illinois soil horizons were subjected to various reduction procedures for the removal of free iron oxides in soils was also determined. Extractable phosphorus, reduction, and x-ray diffraction studies were conducted on concretions from widely separated areas.

Results and Conclusions

Phosphate fractionation studies conducted on five West Virginia soil profiles revealed that the total and organic phosphorus content decreased with depth; the per cent adsorbed phosphorus tended to be greater than the acid-soluble phosphorus in the A horizons, but the reverse was true for the B horizons; and the per cent non-extractable phosphorus tended to be greater in the B than in the A horizons.

Several questions arising from these studies were difficult to answer. Why was adsorbed phosphorus present in the organic horizons; why was non-extractable phosphorus found in some of the highly organic horizons; and why did the sub-surface B horizons with pH values below 6.0 contain more acid-soluble than adsorbed phosphorus?

Extractable phosphorus studies on the Illinois soil profiles revealed that the per cent extractable phosphorus, as determined by the Bray and Kurtz procedure, decreased with depth, reaching a minimum in the B_2 horizons. The amount of extractable phosphorus then increased, reaching a maximum for the profiles in the C horizons. Conversely, the percentage of non-extractable forms of phosphorus reached a maximum in the B_2 and a minimum in the C horizons in all of the Illinois soil profiles studied.

The relative abundance of the non-extractable phosphorus

in various horizons of Illinois soils decreased in the following order:

$$B_2 > B_4 > B_3 > A_2 > C$$

If the zone of maximum clay accumulation is taken as the criterion for locating the B_2 horizons of the Gilpin 1 and 2 soils from West Virginia, the zone of maximum non-extractable phosphorus accumulation, namely, the B_2 horizon, is identical for both the Illinois and West Virginia soils.

For group A and B soils, the B_2 horizon was the only horizon indicating a relationship between degree of maturity and the amount of non-extractable phosphorus. This horizon indicated that, in general, the amount of non-extractable phosphorus tended to increase with increasing soil maturity.

In the group D soils, there appeared to be no relation between soil maturity and the per cent non-extractable phosphorus for the A_2 horizons. On the other hand, a comparison of the extractable phosphorus in the B_2 horizons of the youthful Seaton and youthful Ava series with that of the mature Clinton and mature Ava series indicated that the amount of non-extractable phosphorus also increased with soil maturity, as was true for group A and B soils.

Allaway and Rhoades conducted phosphate fractionation studies on the profile horizons of a number of Nebraska soils, using the procedures of Bray and Kurtz. The high per cent of extractable phosphorus in all horizons except the B of the Butler series, as compared to the results for the West Virginia and Illinois soil profiles, indicated that perhaps less non-extractable phosphorus accumulates in soils developed under calcification, a process giving rise to slightly acid to neutral soils, than is the case where acid leaching occurs, as in podzolization.

It was postulated that the non-extractable phosphorus, in the soils studied, was present as positionally non-extractable phosphorus whose seat was concretionary material. To release this phosphorus, magnesium ribbon-oxalate and sodium hydrosulfite procedures for the removal of free iron oxides in soils were utilized.

Reduction by a magnesium ribbon-oxalate treatment plus one extraction according to the Bray and Kurtz procedure resulted in higher percentages of phosphorus extracted than when the Bray and Kurtz procedure alone was used. There were two exceptions, for which no explanation was apparent.

It was shown that all of the phosphorus was extracted from the C horizons by one treatment with $Na_2S_2O_4$ (pH 2.9 to 3.4) plus one extraction according to the Bray and Kurtz procedure, and from all horizons by $Na_2S_2O_4$ buffered with sodium acetate-sodium tartrate (pH 5.4 to 6.0) plus one extraction according to the Bray and Kurtz procedure. It was also shown that $Na_2S_2O_4$, and not sodium acetate-sodium tartrate, is mainly responsible for the conversion of non-extractable phosphorus into soluble forms.

Dean's and a modified Deb procedure (no sodium hydrosulfite present) extracted about the same per cent of phosphorus, but more than that extracted by the Bray and Kurtz procedure.

Concretions from widely separated areas were found to be very high in phosphorus, and the per cent phosphorus extracted from ball-milled concretions by the procedure of Bray and Kurtz decreased progressively with increasing surface area. Increasing the fluoride ion concentration resulted in greater phosphate ion replacement, but the results indicated that large amounts of NH_4F would be needed to extract all of the phosphorus.

The fluoride ion concentration was sufficient to replace the adsorbed phosphorus in the unground B_2 horizons of the soils included in groups A and B, but with grinding and increased surface area exposure a large concentration of fluoride ion was needed to extract all of the adsorbed phosphorus.

Treating the concretions from Hunt clay and Bluford silt loam with a 4 per cent $Na_2S_2O_4$ solution buffered with sodium acetate-sodium tartrate (pH 5.4 to 6.0) resulted in the extraction of increasing amounts of phosphorus with decreasing sample weight. All of the phosphorus in concretions from

Bluford silt loam, which belongs to the same catena as Cisne silt loam, was extracted when a 0.5-g. sample was used, whereas treating a 0.25-g. sample of concretions from Hunt clay with an 8 per cent $Na_2S_2O_4$ solution buffered with sodium acetate-sodium tartrate (pH 5.4 to 6.0) resulted in extraction of only 71 per cent of the total phosphorus.

The following conclusions were drawn from this study:

1. The zone of maximum non-extractable phosphorus accumulation, in virgin soils subjected to acid leaching, is the horizon of maximum clay accumulation.

2. The per cent non-extractable phosphorus in this horizon tends to increase with increasing soil maturity.

3. All of the non-extractable phosphorus in the soils studied could be extracted with a 4 per cent solution of $Na_2S_2O_4$ buffered with sodium acetate-sodium tartrate (pH 5.4 to 6.0). Deb found that illite and kaolinite were quite stable under reduction by $Na_2S_2O_4$ at pH 2.9 to 3.4 and pH 5.4 to 6.0. A slight reduction, however, in base-exchange capacity (approximately 5 per cent) occurred for montmorillonite. It would appear from these studies that phosphate studies could be conducted on phosphate-free soil systems if a suitable reduction procedure were used.

4. The non-extractable phosphorus in the soils studied is inorganic in nature and is associated with iron and manganese concretionary material as positionally non-extractable phosphorus.

VITA

The author was born on October 11, 1921, in Ford City, Pennsylvania. He was graduated from Har-Brack Union High School, Natrona Heights, Pennsylvania, in 1939. He attended the University of West Virginia from September, 1939, until June, 1942, when he enlisted in the Army. After serving four years, he re-entered the University of West Virginia and in June, 1947, received the degree of Bachelor of Science in Agriculture. The next semester, he entered the Graduate College of the University of West Virginia and in June, 1949, received the degree of Master of Science in Agronomy. The following fall he entered the Graduate College of the University of Illinois. From September, 1950, he was employed as a part-time Research Assistant in the Department of Agronomy.

He is a member of Gamma Sigma Delta and Sigma Xi.